Argonne National Laboratory

DETERMINATION OF METALLIC IMPURITIES AT THE PPB-PPM LEVEL IN SODIUM

by

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Idaho Facilities

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TABLE OF CONTENTS

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

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ABSTRACT

A rapid and reliable method has been developed for separating and determining 13 trace metals in EBR-II sodium. Reactor sodium sampled in a high-purity tantalum cup is vacuum-distilled at 320°C in a quartz distillation unit, and the trace metals in the residue are subsequently determined by atomic-absorption spectrophotometry. Of 15 metals tested, 13 remained quantitatively in the distillation residue, while zinc and cadmium as well as alkali metals distilled with the sodium. Recovery data are presented.

Approximately 2 hr are required to distill 50 g of sodium in the distillation unit. Based on a 50-g sample, the following metals may be determined with a relative precision of ±25% at the levels indicated: aluminum, 600 ppb; bismuth, 100 ppb; calcium, 20 ppb; cobalt, 20 ppb; copper, 20 ppb; chromium, 20 ppb; iron, 50 ppb; magnesium, 5 ppb; manganese, 5 ppb; molybdenum, 70 ppb; nickel, 50 ppb; lead, 50 ppb; and tin, 500 ppb. The distillation residue is also suitable for gamma-ray-spectrometric analysis of fission and activation products that do not distill with the sodium.

I. INTRODUCTION

Analytical methods capable of reasonably rapid determination of trace-element impurities in the ppb-ppm range in sodium metal are urgently needed for monitoring the liquid-metal coolant in fast-reactor plants. Monitoring of trace-metal impurities in the sodium coolant will provide information concerning corrosion of reactor components under actual operating conditions. Such information will be of value to reactor designers and operators. Further, effects of temperature and other variables on corrosion rates of materials of interest may be studied in experimental sodium loops, and results of sodium analysis correlated with observed changes in the test materials. Routine trace-metal analysis of the sodium coolant may uncover unknown accidental contamination, such as the accidental addition of tin and bismuth to the EBR-II sodium coolant from the seal troughs.[1]

DETERMINATION OF METALLIC IMPURITIES
AT THE PPM-PPB LEVEL IN SODIUM

by

T. P. Ramachandran and N. A. Hariland

ABSTRACT

A rapid and reliable method has been developed for separating and determining 13 trace metals in EBR-II sodium. Reactor sodium sampled in a high-purity tantalum cup is vacuum-distilled at 450°C in a quartz distillation unit, and the trace metals in the residue are subsequently determined by atomic-absorption spectrophotometry. Of 15 metals tested, 13 remained quantitatively in the distillation residue, while zinc and cadmium as well as alkali metals distilled with the sodium. Recovery data are presented.

Approximately 2 hr are required to distill 50 g of sodium in the distillation unit. Based on a 50-g sample, the following metals may be determined with a relative precision of ±25% at the levels indicated: aluminum, 600 ppb; bismuth, 100 ppb; calcium, 20 ppm; cobalt, 20 ppb; copper, 20 ppb; chromium, 20 ppb; iron, 50 ppm; manganese, 6 ppb; manganese, 5 ppb; molybdenum, 70 ppm; nickel, 30 ppb; lead, 50 ppb; and tin, 500 ppb. The distillation residue is also suitable for gamma-ray-spectrometric analysis of fission and activation products that do not distill with the sodium.

I. INTRODUCTION

Analytical methods capable of reasonably rapid determination of trace-element impurities in the ppb-ppm range in sodium metal are urgently needed for monitoring the liquid-metal coolant in fast-reactor plants. Monitoring of trace-metal impurities in the sodium coolant will provide information concerning corrosion of reactor components under actual operating conditions. Such information will be of value to reactor designers and operators. Furthter, effects of temperature and other variables on corrosion rates of materials of interest may be studied in experimental sodium loops, and results of sodium analysis correlated with observed changes in the test materials. Routine trace-metal analysis of the sodium coolant may uncover unknown accidental contamination, such as the accidental addition of tin and bismuth to the EBR-II sodium coolant from the seal troughs.

Problems involved in collecting representative sodium samples and analyzing them for trace metals in the ppb-ppm range are rather formidable. Both cesium[2] and iodine[3] have been shown to segregate during sodium sampling; both elements move to the sodium interface when the liquid sodium becomes quiescent before freezing. Since these two elements segregate during sampling, the analyst must assume, in the absence of information to the contrary, that other trace elements may also segregate. Therefore, only analyses made of the entire sodium sample rather than of aliquots can be considered reliable. Contamination associated with dissolution of the sodium sample, neutralization of the resulting highly alkaline solution, solvent extraction, ion exchange, or coprecipitation for separating the trace elements from the sodium matrix, has a high probability of introducing significant analytical errors. In addition, an equivalent acid and reagent blank is difficult, if not impossible, to prepare. Only limited quantities of sodium can be analyzed conveniently by such methods.

Scarborough et al.[4] published a method for determining chromium, manganese, iron, cobalt, and nickel in sodium at 0.1-10 ppm. These metals were coprecipitated with lanthanum hydroxide from small quantities of sodium chloride. Carmichael et al.[5] reported vacuum distillation of sodium for separating iron, nickel, and chromium for atomic-absorption spectrophotometric determination in the range 0.2-4.0 ppm in sodium. Approximately 6 hr were required to distill 10 g of sodium for this analysis.

An ideal method for determining nonvolatile trace metals in sodium would involve collection of a 100-1000-g sodium sample by an overflow technique, in-place separation of the sodium matrix (including ^{24}Na), by vacuum distillation, and transport of the residue in the distillation cup to the laboratory for analysis. This technique would eliminate ^{24}Na decay-time delay, provide reasonably rapid separation of the highly reactive sodium matrix without exposure to the environment, and give the analyst a sample for analysis free of contamination from external sources. The feasibility of the in-place technique requires laboratory proof that trace metals can be successfully separated from sodium by vacuum distillation, and analyzed by a rapid and sensitive method.

This paper describes the determination of 13 nonvolatile trace metals in sodium by vacuum distillation followed by atomic-absorption analysis of the distillation residue. A sample cup made of high-purity tantalum or titanium, selected for induction-heating susceptibility and nonreaction with aqua regia, is filled with sodium in an inert atmosphere by an overflow technique; the cup is then transferred in an inert atmosphere to the laboratory vacuum-distillation unit. Sodium is removed by vacuum distillation and the residue prepared in 4% V/V concentrated hydrochloric acid-ethyl alcohol for the determination of Al, Ca, Cr, Co,

Cu, Mg, Mn, Mo, Ni, and Fe, and in an aqueous solvent for the determination of Sn, Pb, and Bi by atomic-absorption spectrophotometry.

Although not covered specifically in this paper, the distillation residue is also useful for gamma-ray-spectrometric analysis of nonvolatile fission and activation products in the sodium coolant of a reactor.

II. APPARATUS

A. Sampling Equipment

Sodium samples for laboratory distillation are taken in cups of high-purity tantalum or titanium in an inert atmosphere by an overflow technique. Figure 1 is a schematic diagram of the sampling device. The tantalum cup, cleaned with hydrofluoric acid and aqua regia, is placed inside the resistance-heated sampling pot so that the inlet sodium line extends near the top edge of the cup. The sampling pot is sealed, purged with argon, and then installed in the sodium-sampling line. Sodium inlet and outlet valves are opened, and sodium flow is established through the tantalum cup at approximately one liter/min. Argon-gas pressure is adjusted to force the overflow sodium to drain from the bottom of the pot. After sodium has flowed through the cup for the desired period, normally 15 min, the inflow of sodium is stopped and the argon pressure is adjusted to blow any residual sodium from the sampling pot. The outlet valve is closed, and the heaters are turned off.
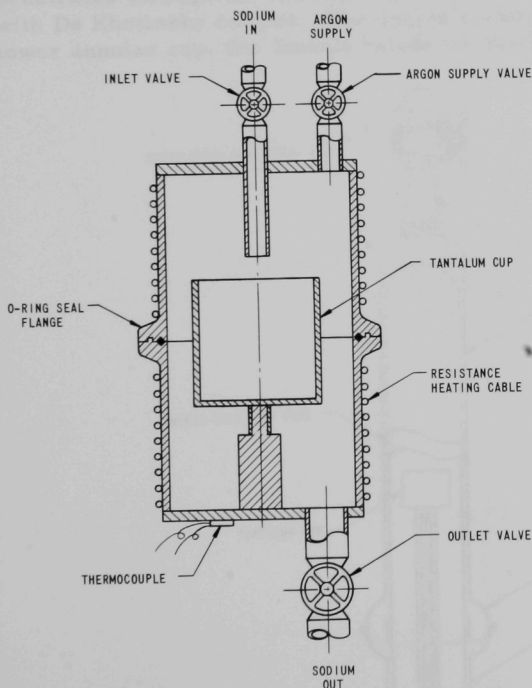
Fig. 1. Schematic Diagram of Sampling Device.
ANL Neg. No. ID-103-L5510.

After the sodium sample has cooled to ambient temperature, the pot is pressurized slightly with argon and disconnected from the sampling line.

II. APPARATUS

A. Sampling Equipment

Fig. 1. Schematic diagram of sampling device.

The entire sampling pot is then carried to the laboratory, where it is opened in an inert atmosphere, and the sample cup is transferred to the distillation equipment. When radioactive sodium from the reactor primary loop is sampled, the ^{24}Na activity is allowed to decay for five days before disconnecting the sampling pot from the sampling line.

B. Distillation Unit

The distillation unit, shown in Fig. 2, is made of quartz, except for the upper stopcock, which is Pyrex. The body of the unit could be also made of Pyrex; however, the condenser tube should be quartz. Each sample cup has a short, hollow tailpiece which serves two purposes: (1) alignment and rigid support on the hollow quartz pedestal in the distillation unit, and (2) acceptance of the Chromel-Alumel thermocouple, which extends through the center of the quartz-tube support. The thermocouple penetrates through the bottom of the unit, where it is sealed and reinforced with De Khotinsky cement. The quartz condenser tube, which rests on a lower annular cup, fits loosely inside the distillation unit, as shown in Fig. 2.
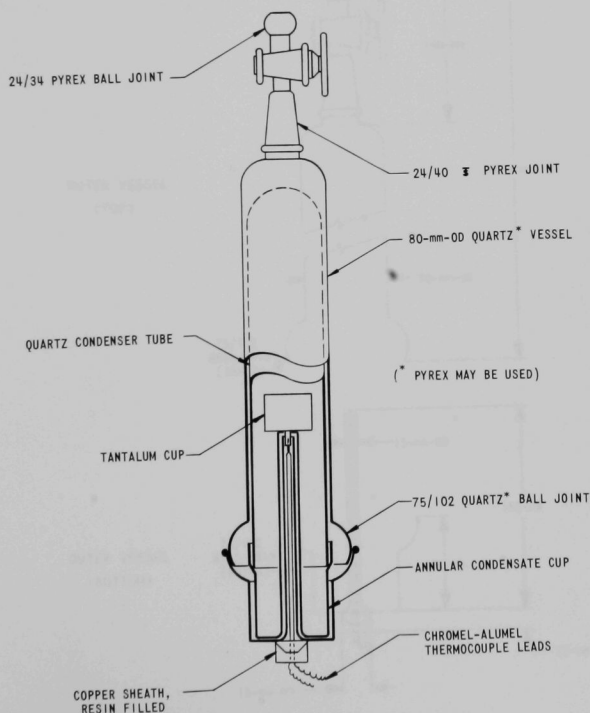
Fig. 2. Unit for Sodium Distillation

The entire samples pot is then carried to the laboratory, where it is reposed in an inert atmosphere, and the sample cup is transferred to the distillation equipment. When radioactive sodium from the regular primary loop is sampled, the ^{24}Na activity is allowed to decay for five days before disconnecting the sampling pot from the sampling line.

B. Distillation Unit

The distillation unit, shown in Fig. 2, is made of quartz, except for the upper stopcock, which is Pyrex. The body of the unit could be also made of Pyrex; however, the condenser tube should be quartz. Each sampling cup has a short, in-flow tail-tube which serves two purposes: (1) alignment and rigid support on the hollow quartz pedestal in the distillation unit, and (2) acceptance of the thermocouple, since the thermocouple-which extends through the center of the quartz tube, support... The thermocouple penetrates through the bottom of the quartz tube, where it is sealed and cemented with De Khotinsky cement. The quartz condenser tube, which rests on a lower sample cup, fits loosely inside the distillation unit, as shown in Fig. 3.

Fig. 2. Unit for sample distillation

The condenser tube provides the surface on which distilled sodium condenses, and the lower annular cup collects the sodium that flows from the condenser tube. Distilled sodium can be removed readily from the distillation unit by removing the condenser tube and the annular cup. Figures 3 and 4 show the dimensions of the distillation apparatus.

Figure 5 shows the distillation unit assembled for operation. Induction heating is supplied through a water-cooled copper tube formed into a 3.5-in.-dia coil, which closely fits the outside of the distillation unit. Maximum output of the induction power supply is 2.5 kW at 450 kHz. A Pirani gauge is used to measure the vacuum within the system, and the distillation temperature is recorded on a strip-chart recorder. For safety during distillation, the unit is enclosed in an inert atmosphere.

Fifty grams of sodium can be distilled in approximately 2 hr at a temperature of 280-320°C and a pressure of 1-5 μ.

Fig. 3. Dimensions of the Distillation Unit

The condenser acts, providing the surface on which the distilled sodium condenses, and the lower reaches cup collects the sodium in that flows from the condenser tube. Distilled sodium can be recovered later from the distillation unit by removing the condenser tube and the collection cup. Figures 3 and 4 show the dimensions of the distillation apparatus.

Figure 3 shows the distillation unit assembled for operation. Induction heating is supplied through a water-cooled copper tube formed into a 4.5-in.-dia coil, which closely fits the outside of the distillation unit. Maximum output of the induction power supply is 2.5 kW at 450 kHz. A Pirani gauge is used to measure the pressure within the system, and the distilled temperature is recorded on a watch-chart recorder. For safety during distillation, the unit is enclosed in an inert atmosphere.

Fifty grams of sodium can be distilled in approximately 2 hr at a temperature of 280–350°C and a pressure of 15 μ.

Fig. 3. Dimensions of the distillation Unit.

CONDENSER TUBE

66-mm-OD

230-mm

50.8-mm-OD

47.0-mm-ID

40.6-mm

56.5-mm

8.47-mm-OD

12.7-mm

CONDENSATE CUP

28-mm-OD

70-mm-OD

182-mm

108-mm

66-mm

28.6-mm

.635-mm-OD
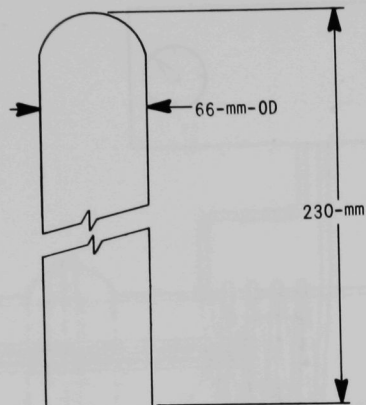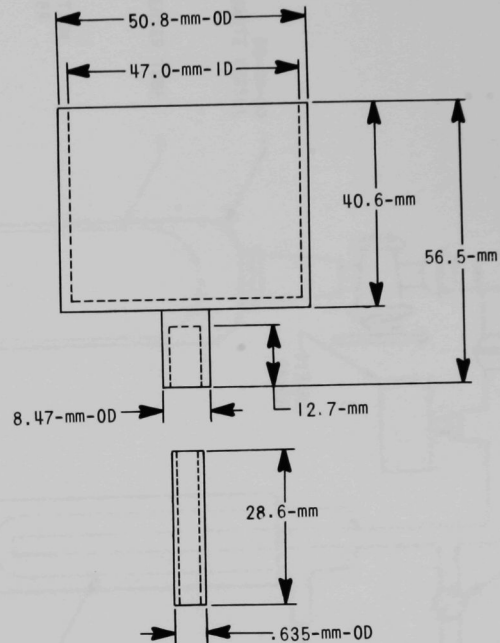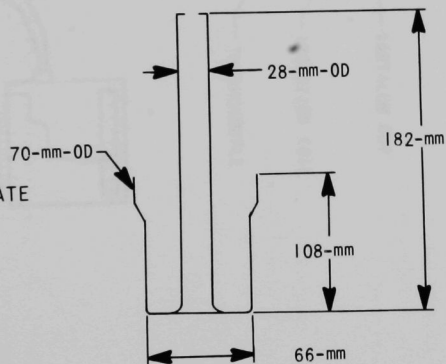
TANTALUM CUP & T.C. WELL

Fig. 4. Dimensions of the Condenser System and Tantalum Cup

PRESSURE
GAUGE

HELIUM
SUPPLY

PIRANI
GAUGE

TO
VACUUM
PUMP

80-mm-OD
QUARTZ VESSEL

CONDENSER TUBE

COLD TRAP

INDUCTION
HEATER

TANTALUM CUP

INDUCTION COIL

THERMOCOUPLE

RECORDER
TEMP vs TIME
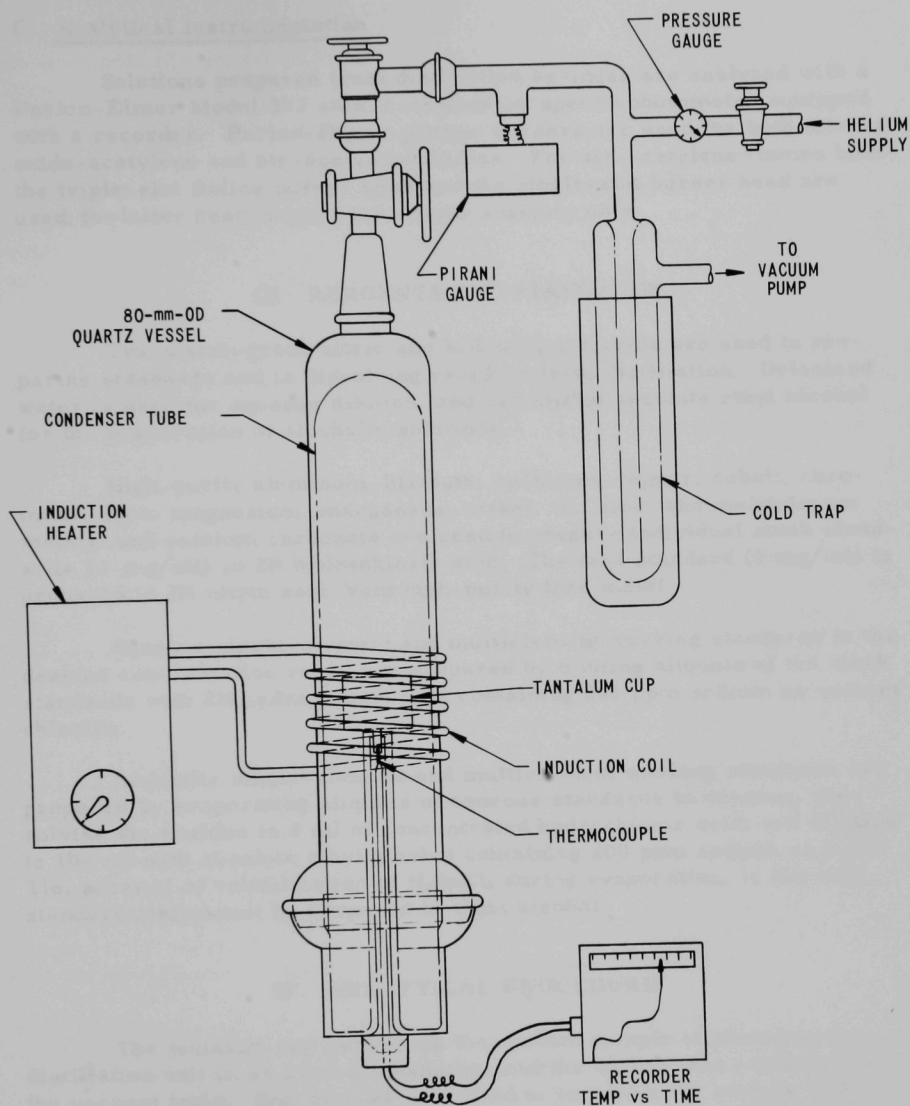
Fig. 5. Assembly for Vacuum Distillation.
ANL Neg. No. ID-103-L5512.

Fig. 5. Apparatus for vacuum purification.
AML Neg. No. 42,210-38-36.

C. Analytical Instrumentation

Solutions prepared from distillation residues are analyzed with a Perkin-Elmer Model 303 atomic-absorption spectrophotometer equipped with a recorder. Perkin-Elmer premix burners are used for both nitrous oxide-acetylene and air-acetylene flames. For air-acetylene flames both the triple-slot Boling burner head and the single-slot burner head are used; the latter head is used for copper analysis only.

III. REAGENTS AND STANDARDS

Transistor-grade nitric and hydrochloric acids are used in preparing standards and in dissolving residues from distillation. Deionized water is used for aqueous dilution, and redistilled absolute ethyl alcohol for the preparation of alcoholic solutions.

High-purity aluminum, bismuth, cadmium, copper, cobalt, chromium, iron, magnesium, manganese, nickel, tin, zinc, and molybdenum metals, and calcium carbonate are used to prepare individual stock standards (1 mg/ml) in 2N hydrochloric acid. The lead standard (1 mg/ml) is prepared in 2N nitric acid from high-purity lead metal.

Aqueous single-element and multielement working standards in the desired concentration range are prepared by diluting aliquots of the stock standards with 2N hydrochloric acid containing 200 ppm sodium as sodium chloride.

Alcoholic single-element and multielement working standards are prepared by evaporating aliquots of aqueous standards to dryness, dissolving the residue in 4 ml of concentrated hydrochloric acid, and diluting to 100 ml with absolute ethyl alcohol containing 200 ppm sodium as NaCl. Tin, because of volatilization of H_2SnCl_6 during evaporation, is the only standard that cannot be prepared in ethyl alcohol.

IV. ANALYTICAL PROCEDURE

The tantalum cup containing the sodium sample is placed in the distillation unit in an inert atmosphere, and the unit is then connected to the vacuum train. Enough heat is applied to just melt the sodium in the cup. The system is then evacuated and the molten sodium allowed to degas before further heat is applied. The power is then adjusted so that the rate of temperature rise is approximately 20°C/min until distillation begins. The course of the distillation is followed by observing the temperature-time record, and the temperature is maintained at 280°-320°C. When the distillation is complete, the temperature rises sharply, heating is

Solutions prepared from mineralization residues are analyzed with a
Perkin-Elmer Model 303 atomic-absorption spectrophotometer equipped
with a recorder. Perkin-Elmer Premix burners are used for both nitrous
oxide-acetylene and air-acetylene flames. For air-acetylene flames both
the triple-slot Boling burner head and the single-slot burner head are
used; the latter head is used for copper analysis only.

III. REAGENTS AND STANDARDS

Reagent-grade nitric and hydrochloric acids are used in pre-
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water is used for aqueous dilution, and reagent-grade absolute ethyl alcohol
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High-purity aluminum, bismuth, cadmium, copper, cobalt, chro-
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prepared in 2N nitric acid from high-purity lead metal.

Aqueous single-element and multielement working standards in the
desired concentration range are prepared by diluting aliquots of the stock
standards with 2N hydrochloric acid containing 500 ppm sodium as sodium
chloride.

Alcoholic single-element and multielement working standards are
prepared by evaporating aliquots of aqueous standards to dryness, dis-
solving the residue in 4 ml of concentrated hydrochloric acid, and diluting
to 100 ml with absolute ethyl alcohol containing 200 ppm sodium as NaCl.
Tin, because of volatilization of its chloride during evaporation, is the only
standard that cannot be prepared in ethyl alcohol.

IV. ANALYTICAL PROCEDURE

The isolated cup containing the sodium sample is placed in the
distillation unit in an inert atmosphere, and the unit is then connected to
the vacuum train. Enough argon is admitted to just melt the sodium in the
cup. The system is then evacuated and the molten sodium allowed to degas
below ignition heat is applied. The power is then adjusted so that the rate
of temperature rise is approximately 20°C/min until distillation begins.
The course of the distillation is followed by observing the temperature-
time record, and the temperature is maintained at 600-900°C. When the
distillation is complete, the temperature rises sharply, heating is

discontinued, and the system is allowed to cool to room temperature. The vacuum pump is shut off, and the system is brought to atmospheric pressure by bleeding in helium.

The distillation unit is removed from the vacuum train, and the tantalum cup is carefully removed. The residue in the cup is treated with 1.5 ml of aqua regia, diluted with 4 ml of water, and heated on a steam bath for approximately 5 min. The solution is then transferred to a 25-ml volumetric flask with a transfer pipet, and the cup is washed several times with 2N hydrochloric acid. The sample is then diluted to 25 ml with 2N hydrochloric acid.

Five milliliters of the solution is pipetted from the 25-ml flask and reserved for analysis of tin, lead, and bismuth in an aqueous medium. The remaining solution is evaporated to dryness, 1 ml of concentrated hydrochloric acid is added to the residue, and the solution is diluted to volume with ethyl alcohol.

The prepared solution and a procedure blank are analyzed by atomic-absorption spectrophotometry for the concentration of individual metallic constituents. Calibration curves are prepared for each metal from standard solutions of similar composition run concurrently with the sample and blank. The total quantity of each trace metal in the unknown solution is calculated and reported as ppm in the original sodium sample taken for analysis.

Multielement standards containing appropriate quantities of Ca, Co, Cr, Cu, Fe, Mn, Mg, Mo, and Ni in 4% V/V hydrochloric acid-ethyl alcohol containing 200 ppm sodium as NaCl are used for analysis of unknown samples prepared in the same solvent. Aqueous standards of Bi, Pb, and Sn spiked with 200 ppm NaCl are used for analysis of these metals. Aluminum is not included in the multielement standards because it enhances the absorption of molybdenum and suppresses that of calcium. Aluminum is prepared and used as a single-element standard in the alcoholic medium. If aluminum is present in sodium samples, its effect on calcium can be eliminated by adding lanthanum (100 ppm) to the sample.

Table I lists instrumental parameters used for the various trace metals studied in this work. Although these values may not apply to other instruments, they may serve as a general guide.

TABLE I. Instrumental Parameters for Atomic Absorption in Alcoholic Medium

Hollow-cathode Lamp Used	Lamp Current, mA	Wavelength, Å	Slit Width, mm	Burner Type	Height of Beam above Burner, mm	Flame Oxidant-Fuel	Flowmeter Readings, Arbitrary Units	
							Fuel	Oxidant
Copper	30	3247	4	Single-slot	9	Air-C_2H_2	5.0	5.0
Cobalt	30	2407	3	Triple-slot	7	Air-C_2H_2	5.0	5.0
Chromium	30	3579	3	Triple-slot	7	Air-C_2H_2	6.0	6.0
Manganese	30	2800	4	Triple-slot	7	Air-C_2H_2	6.0	6.0
Nickel	30	2320	3	Triple-slot	7	Air-C_2H_2	5.0	5.5
Calcium	18	4227	3	Triple-slot	14	Air-C_2H_2	6.5	7.0
Magnesium	18	2852	4	Triple-slot	7	Air-C_2H_2	5.0	5.5
Aluminum	18	3093	3	Nitrous oxide	12	N_2O-C_2H_2	6.0	6.5
Molybdenum	25	3133	3	Nitrous oxide	12	N_2O-C_2H_2	6.0	6.0
Lead	30	2833	4	Triple-slot	7	Air-C_2H_2	5.0	5.0
Bismuth	30	2231	3	Triple-slot	7	Air-C_2H_2	5.0	5.0
Iron	30	2483	3	Triple-slot	7	Air-C_2H_2	5.0	6.0
Tin	30	2863 and 2246	4	Nitrous oxide	7	N_2O-C_2H_2	6.0	7.0
Cadmium	12	2288	4	Triple-slot	7	Air-C_2H_2	5.0	6.0
Zinc	12	2138	4	Triple-slot	14	Air-C_2H_2	5.0	5.5

V. DISCUSSION AND RESULTS

A. Effect of Solvent Composition on Atomic-absorption Measurements of Trace Metals

Fifteen metals (Al, Bi, Ca, Co, Cu, Cr, Fe, Mg, Mn, Mo, Ni, Pb, Sn, Zn, and Cd) were studied in both aqueous and alcoholic solution with and without sodium present to determine the optimum medium for their determination by atomic-absorption techniques.

In aqueous media, the atomic absorption of Cu (4 ppm), Sn (21 ppm), Mg (1 ppm), Ni (4 ppm), and Co (4 ppm) was not significantly influenced by sodium concentrations between 15 and 5000 ppm of sodium. However, Mn (2 ppm), Cr (2 ppm), Pb (10 ppm), Fe (5 ppm), Bi (10 ppm), and Ca (2 ppm) in aqueous solution showed a maximum absorption enhancement of 5-10% up to 60 ppm of sodium, but then no further change to 2000 ppm of sodium. Molybdenum showed a maximum absorption suppression of approximately 10% absorption up to 100 ppm of sodium, and then no further change to 2000 ppm of sodium.

Under our distillation conditions, the residue contains approximately 5 mg of sodium for 50 g of sodium distilled. If the atomic-absorption analysis is to be made on aqueous solutions, 500 ppm of sodium are added to all aqueous standards to closely approximate the sodium content of the aqueous solutions prepared from distillation residues and minimize errors (10% maximum suppression or enhancement) associated with sodium concentrations.

DISCUSSION AND RESULTS

A. Effect of Anion Composition on Atomic-Absorption Measurements of Trace Metals

Fifteen metals (Al, Bi, Ca, Cd, Co, Cr, Fe, Hg, Mn, Mo, Ni, Pb, Sn, Zn, and Cu) were studied in high-aqueous and alcohol solution with and without sodium present in a relatively uniform manner for their determination by atomic-absorption techniques.

In concentrations in the sample absorption of trace metals, Sn (5 ppm), Mg (1 ppm), Al (1 ppm), and Cr (1 ppm) were not significantly influenced by sodium-concentration range between 15 and 2000 ppm of sodium. However, Mn (2 ppm), Cr (5 ppm), Pb (10 ppm), Sn (5 ppm), Bi (10 ppm), and Cu (2 ppm) in aqueous solution showed a maximum absorbance range gradually from 5-10% up to 60 ppm of sodium but then no further decrease to 2000 ppm of sodium. Molybdenum showed a maximum absorption suppression of approximately 10% absorption up to 100 ppm of sodium, and then no further decrease to 2000 ppm of sodium.

Under any distillation conditions, the residue contains approximately 8 mg of sodium for 50 ml of medium distilled. If the atomic-absorption analysis is to be based on aqueous solutions 500 ppm of sodium are added to all aqueous standards to offset, approximately, the sodium content of the aqueous solutions prepared (all distillation products and mixtures of the HNO3 maximum suppression of instrumental association) 10 million-fold concentration.

Further study showed that the absorption of trace metals increased by a factor of 2 to 3 with no increase in flame noise when they were analyzed in 4% V/V hydrochloric acid-ethyl alcohol compared to the absorption obtained in the aqueous medium. Although the influence of sodium concentration in the alcohol medium appears to be even less than in the aqueous medium, all standards are prepared in 4% V/V hydrochloric acid-ethyl alcohol containing 200 ppm sodium to closely approximate the solutions prepared from distillation residues.

The method described under Analytical Procedure uses the alcoholic solvent for all trace metals other than tin, bismuth, and lead, since it permits analysis at levels approximately one-third to one-half of those obtainable in an aqueous medium. For samples containing proportionately higher concentrations of trace metals, the aqueous medium may be used advantageously.

Table II lists useful standard calibration ranges and lower limits of analysis for the determination of 13 trace metals in sodium. Tin, bismuth and lead, included in the table, are analyzed in an aqueous medium.

TABLE II. Calibration Ranges and Lower Limits of Analysis

Element	Medium	Calibration Range: Metal Concentration, ppm	Analytical Limit at 25% Precision (50 g of Sodium), ppm
Aluminum	Alcoholic	1 to 10	0.6
Bismuth	Aqueous	0.2 to 2.5	0.1
Calcium	Alcoholic	0.04 to 0.12	0.02
Cobalt	Alcoholic	0.04 to 0.24	0.02
Chromium	Alcoholic	0.024 to 0.12	0.02
Copper	Alcoholic	0.04 to 0.24	0.02
Iron	Alcoholic	0.08 to 0.32	0.05
Magnesium	Alcoholic	0.01 to 0.1	0.005
Manganese	Alcoholic	0.008 to 0.048	0.005
Molybdenum	Alcoholic	0.12 to 0.5	0.07
Nickel	Alcoholic	0.08 to 0.32	0.05
Lead	Aqueous	0.1 to 15	0.05
Tin	Aqueous	0.8 to 30	0.5

B. Recovery of Trace Metals

Recovery studies were made for the 15 metals to establish whether they remain quantitatively in the residue from distillation or codistill with the sodium. Of the 15 metals tested only zinc and cadmium distilled with the sodium; more than 95% of each of the other 13 metals remained in the residue.

Aliquots of standard solutions containing microgram quantities of the metal chlorides were pipetted into a tantalum cup and carefully evaporated to dryness; then approximately 10 g of sodium, containing essentially non-detectable quantities of trace metals, were added to the cup in an inert atmosphere. Sodium reduces all metal chlorides to metals; however, aluminum, calcium, chromium, and magnesium are converted to their respective oxides by reaction with the sodium oxide present as a contaminant in sodium metal. The sodium was distilled and the residue analyzed for each trace metal. Since microgram quantities of zinc and cadmium appeared to codistill with the sodium, the test was repeated for these two metals using carrier-free radioactive tracers. The zinc and cadmium tracers were found in the distilled sodium. Tin and iron were also added as radioactive tracers and remained quantitatively in the distillation residue. Table III shows the results of the study.

TABLE III. Recovery of Trace-metal Chlorides Added to Sodium

Metal	Micrograms Added	Percent Recovered		
		Exp. 1	Exp. 2	Exp. 3
Aluminum	60	100	100	100
Bismuth	108	94	95	
Calcium	10	106	109	
Cadmium	10	50	27	
Cadmium-109	carrier free		4	0
Chromium	20	100	99	
Cobalt	40	97	99	
Copper	40	101	99	
Iron	45	99	100	
Iron-59	trace carrier	100	99	
Lead	120	100	98	102
Magnesium	20	96	99	
Manganese	8	100	100	
Molybdenum	58	101	100	
Nickel	40	103	97	
Tin-113	trace carrier	98	99	
Zinc	10	60	50	
Zinc-65	carrier free			20

Note: Approximately 10 g of sodium was added to trace metals as chlorides in tantalum cup and vacuum distilled.

The recovery of trace metals in the residue from vacuum distillation of sodium was studied further. Microgram quantities of metal powders were thoroughly mixed with 50 g of sodium in a titanium cup and then vacuum distilled. Both the residue and the sodium distillate were analyzed for trace-metal content. The distillation residues were dissolved in acid and analyzed

by atomic absorption. The sodium distillate was dissolved and acidified, and the metals after separation by 8-hydroxyquinoline extraction or by coprecipitation were determined by atomic absorption against an equivalent acid and reagent blank. The residue recoveries were calculated by dividing the trace metal found in the residue by the sum of that found in the residue and the distillate. Table IV presents the results of such a recovery study.

TABLE IV. Recovery of Trace Metals Added to Sodium

Metal	Experiment 1: Trace metals added as powders to 50 g of sodium			Experiment 2: Trace metals from 50 g of EBR-II sodium		
	ppm in the Residue	ppm in the Distilled Sodium[a]	Percent Recovery in the Residue	ppm in the Residue	ppm in the Distilled Sodium[a]	Percent Recovery in the Residue
Aluminum	1.10	<0.03	>97			
Bismuth				2.4	n.d.	100
Calcium	0.20	n.d.	100			
Chromium	0.4	n.d.	100	0.11	<0.01	>92
Cobalt	0.52	0.014	97			
Copper	0.126	0.006	95	0.02	<0.003	>87
Iron	0.80	0.02	98	0.11	<0.02	>85
Lead	0.81	0.10	89	8.2	0.78	91
Magnesium	0.30	n.d.	100			
Manganese	0.31	0.005	98			
Molybdenum	0.74	n.d.	100			
Nickel	0.47	0.013	97			
Tin				19.5	n.d.	100

[a]Maximum values based on minimum detectable quantities.
n.d. - not detected.

The distillation recovery of some of the trace metals present in the EBR-II primary and secondary sodium was established by distilling a 50-g sodium sample, and analyzing both the distilled sodium and the residue for trace-metal content. Table IV includes the results of this additional study. Considering the magnitude of error involved in the analyses of trace metals in the distilled sodium with respect to an equivalent acid and reagent blank, the recoveries shown are reasonably good.

Known quantities of 11 of the metals studied were added simultaneously to 10 g of sodium. The sodium was vacuum-distilled, and the residue was analyzed according to the method described under Analytical Procedure. Table V shows results of the analysis for two similarly spiked samples.

TABLE V. Determination of 11 Trace-metal Chlorides
Added Simultaneously to Sodium (analysis
of residue after vacuum distillation)

Metal	Metal Added, ppm in Sodium	Metal Found, ppm in Sodium
Bismuth[a]	1.08	1.19
	0.54	0.50
Calcium	0.44	0.40
	0.8	0.88
Chromium	0.2	0.2
	0.2	0.15
Copper	0.4	0.46
	0.2	0.20
Cobalt	0.4	0.45
	0.2	0.21
Iron	0.4	0.46
	0.4	0.40
Magnesium	0.2	0.23
	0.08	0.10
Manganese	0.08	0.095
	0.04	0.040
Lead[a]	1.25	1.25
	0.65	0.60
Nickel	0.4	0.4
	0.4	0.41
Tin[a]	4.15	4.15
	10.45	10.7

[a] Tin, lead, and bismuth are determined by atomic-
absorption spectrophotometry in aqueous medium.

Residue for analysis provided by vacuum distillation
of 10 g of sodium spiked with above metals as
chlorides.

Results from the recovery test and the spiked sodium samples indi-
cate that distillation of sodium followed by atomic-absorption analysis of
the residue may be successfully used for the determination of Al, Bi, Ca,
Cr, Co, Cu, Pb, Mg, Mn, Mo, Ni, Fe, and Sn in the ppb-ppm range in sodium.

TABLE V. Determination of 17 Trace-metal Chlorides
Added Simultaneously to Sodium (analysis
of residue after vacuum distillation)

Metal	Metal Added, ppm in Sodium	Metal Found, ppm in Sodium
Bismuth[a]	1.08	1.19
	0.54	0.50
Calcium	0.44	0.40
	0.8	0.88
Chromium	0.2	0.2
	0.2	0.15
Copper	0.2	0.16
	0.2	0.20
Cobalt	0.2	0.15
	0.2	0.21
Iron	0.2	0.2
	0.2	0.20
Magnesium	0.2	0.23
	0.05	0.10
Manganese	0.08	0.095
	0.04	0.030
Lead[a]	1.25	1.25
	0.45	0.60
Nickel	0.2	0.2
	0.2	0.41
Tin[a]	3.15	4.15
	10.45	10.7

[a]Tin, lead, and bismuth are determined by atomic-
absorption spectrophotometry in aqueous medium.

Residue for analysis provided by vacuum distillation
of 10 g of sodium spiked with above metals as
chlorides.

Results from the recovery test and the spiked sodium samples indi-
cate that distillation of sodium followed by atomic-absorption analysis of
the residue may be successfully used for the determination of Al, Bi, Ca,
Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Fe, and Sn in the ppb-ppm range in sodium.

C. Trace Metals in EBR-II Sodium

The analytical method described has been applied to the analysis of 50-g samples of EBR-II primary and secondary sodium. Tables VI and VII list results which are typical for both the primary and the secondary sodium. All less-than values represent the practical lower limit of the method. Aluminum, cobalt, and molybdenum are not detectable in EBR-II sodium. Manganese is detectable around 0.005 ppm.

TABLE VI. Trace Metals in EBR-II Primary Sodium

Metal	Trace Metals in Sodium, ppm		
	7/11/69	7/28/69	8/21/69
Aluminum	<0.6	<0.6	<0.6
Bismuth	2.0	2.1	1.8
Calcium	0.09	0.05	0.02
Chromium	0.04	0.025	0.02
Cobalt	<0.02	<0.02	<0.02
Copper	0.1	0.02	<0.02
Iron	0.25	0.06	0.14
Lead	10.8	11.7	11.0
Magnesium	0.04	0.06	0.01
Manganese	<0.005	<0.005	<0.005
Molybdenum	<0.07	<0.07	<0.07
Nickel	0.05	<0.05	<0.05
Tin	25.6	24.5	22.4

TABLE VII. Trace Metals in EBR-II Secondary Sodium

Metal	Trace Metals in Sodium, ppm		
	7/11/69	7/29/69	8/21/69
Aluminum	<0.6	<0.6	<0.6
Bismuth	<0.1	<0.1	<0.1
Calcium	0.05	<0.02	<0.02
Chromium	0.06	0.035	0.02
Cobalt	<0.02	<0.02	<0.02
Copper	0.07	0.02	<0.02
Iron	0.8	0.1	0.1
Lead	0.2	0.7	0.7
Magnesium	0.01	0.02	0.02
Manganese	<0.005	0.005	0.008
Molybdenum	<0.07	<0.07	<0.07
Nickel	0.1	<0.05	<0.05
Tin	<0.5	<0.5	<0.5

Tin and bismuth concentrations in the primary sodium are the result of a postulated seal-trough spill that occurred in July 1965. Copper in the primary system originated principally from partial dissolution of unclad bus bars prior to March 1967.[6] The source of the lead is unknown, but lead was not present in the as-charged sodium, since the sodium source was the same for both sodium systems.

VI. SUMMARY

The method described in this paper provides for reasonably rapid separation and analysis of 13 trace metals in the ppb-ppm range in reactor sodium metal. The method is readily adaptable to analysis of residues from in-line distillation, which would remove essentially all the radioactive sodium and eliminate the cooling time required for health-physics reasons before laboratory distillation. In-line distillation for trace-metal analysis is being actively pursued.

Since the trace metals are collected from the entire sample, any segregation that may occur in the sample is not a problem, as the sample is not aliquoted before analysis.

ACKNOWLEDGMENT

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